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Rahul B. Kawthekar^a & Geon-Joong Kim^a ^a Department of Chemical Engineering, Inha University, Incheon, South

Korea

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Hydrolytic Kinetic Resolution of Terminal Epoxides catalyzed by Novel Bimetallic Chiral Co (Salen) Complexes

Rahul B. Kawthekar and Geon-Joong Kim

Department of Chemical Engineering, Inha University, Incheon South Korea

Abstract: Novel bimetallic chiral Co (salen) complexes bearing transition-metal salts have been synthesized. The easily prepared complexes exhibited very high catalytic reactivity and enantioselectivity in hydrolytic kinetic resolution (HKR) of racemic terminal epoxides and consequently provided enantiomerically enriched epoxides (up to 99% ee).

Keywords: Asymmetric catalysis, chiral bimetallic complexes, hydrolytic kinetic resolution, terminal epoxides

INTRODUCTION

Catalytic asymmetric epoxidation is one of the most direct and valuable methods for the asymmetric synthesis of bioactive molecules.^[1] Numerous efforts in this field have resulted in the establishment of highly efficient catalytic methods using the Sharpless epoxidation,^[2] enzymatic kinetic resolutions,^[3] and hydrolytic kinetic resolution (HKR),^[4] which provide a wide range of optically active epoxides.^[5] Among the available methods,^[6] HKR is an effective and simple method for the preparation of optically active epoxides.^[7–9] In our previous research, we have shown that dimeric chiral salens bearing 13 group metal salts displayed good enantioselectivity and reactivity for the asymmetric kinetic resolution of terminal epoxides.^[10]

Address correspondence to Geon-Joong Kim, Department of Chemical Engineering, Inha University, Incheon 402751, South Korea. E-mail: kimgj@inha.ac.kr

HKR of Racemic Terminal Epoxides



Scheme 1. Chiral Co(salen) complexes.

Pursuant to our own efforts directed toward designing bimetallic chiral Co (salen) catalysts, we report herein highly enantioselective HKR of racemic terminal epoxides catalyzed by easily synthesized bimetallic chiral Co (salen) catalysts containing transition-metal salts. They have never been exploited as catalysts in asymmetric synthesis of chiral building blocks. However, these types of salen catalysts are remarkably efficient and enantioselective in HKR of terminal epoxides in this work (Scheme 1).

EXPERIMENTAL

General Procedure for Catalyst Preparation

The bimetallic chiral Co (salen) complexes were synthesized by mixing 1:1.2 molar ratio of chiral salen (R,R)-(-)-N,N-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diamino cobalt (II) and transition-metal salts in tetrahydro-furan (THF), and the mixture was stirred in an open atmosphere for 2 h. After the reaction, the solvent was removed under reduced pressure and the final product (catalyst) was collected by dissolution in methylene chloride (MC) to remove the unreacted metal salts. After evaporation of MC solvent, a dark green and dark brown solid powder was obtained in the yield of 95–98%.

General Procedure for Hydrolytic Kinetic Resolution (HKR)

In a representative reaction of HKR, (\pm) -epichlorohydrine (1 g, 0.01 mol, 1.0 equiv.) and catalyst (*R*, *R*)-**a** (0.023 g, 0.3 mol%) were charged in an ovendried 25-ml flask, and the reaction mixture was stirred at room temperature. After complete dissolution of catalyst, H₂O (0.106 g, 0.55 equiv.) was added dropwise, and the resultant reaction mixture was stirred until optically pure terminal epoxides occurred. The recovered epoxide was filtered through an MgSO₄ pad after reaction. The optically pure product was isolated by Kugelrohr distillation (Eyela KRD100, Tokyo Rikakikai Co. Ltd.) into a receiving flask at 0 °C. An enantiomeric excess of the recovered epoxide was determined by gas chromatography (GC) equipped with a chiral capillary column.

Materials

(R,R)-(-)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diamino cobalt (II) [or (salen)Co^{II}] was purchased from Aldrich. THF, MC, and n-hexane were used after distillation. Transition-metal salts and all other reagents were purchased from Aldrich, Fluka, and TCI.

Analysis

All ¹H NMR and ¹³C NMR were recorded using a 400-MHz FT NMR spectrophotometer (Varian Unity Nova 400) at ambient temperature. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 series II instruments equipped with flame ionization detector (FID) detectors using a chiral column [Chiraldex G-TA and A-TA, 20 m × 0.25 mm i.d. (Astec) and HP 3396 integrators with HP Chem Station software for data analysis]. Chiral HPLC analyses were performed on a Younglin instrument using a Chiralcel[®] OD column (24 cm \times 0.46 cm i.d.; Chiral Technologies, Inc.) and (R,R)-Whelk-O1/(S,S)-Whelk-O1 column (24 cm \times 0.46 cm i.d.) (Regis) at 254 nm. Extended X-ray absorption fine structure (EXAFS) values were measured by a Rigaku Model R-XAS (Rigaku, Japan) applying Co K-edge energy (7708.9 eV), Ni K-edge energy (8332.8 eV), and Fe K-edge energy (7112.0 eV) radiation, and data were simulated using a FEFF6 (FEFF) program. Electron spectrosopy for chemical analysis (ESCA) data were obtained with a Sigma Probe (Thermo VG, U.K.) spectrometer using Mg K α radiation as an excitation source (hv = 1253.6 eV). Binding energy was compared with a reference of cobalt salt such as Co(II) salen and Jacobsen catalyst purchased from Aldrich. Electronspray ionisation mass spectroscopy (ESI-MS) analysis was recorded on Micromass Quattro LC equipped with electron spray (Nanoflow ESI).

RESULTS AND DISCUSSION

A series of chiral Co (salen) complexes (Scheme 1) were screened to identify the most enantioselective and reactive catalyst in the hydrolytic kinetic resolution (HKR) of (\pm) -epichlorohydrine (ECH) with H₂O as a nucleophile (Table 1). As can be seen from Table 1, chiral Co (salen) complexes 1, 4, 5, and 7 were found to be much more active and enantioselective than 2, 3, and 6 complexes. Furthermore, the catalysts 1, 4, and 5 were identified as the most effective among the catalytic series, and they were selected for further study. The HKR of (\pm) -ECH was investigated using the chiral

HKR of Racemic Terminal Epoxides

Table 1. Optimization of chiral Co (salen) complexes in asymmetric HKR of (\pm) -ECH

Cl $(+)$ H_2O	(<i>R</i> , <i>R</i>)-Cat. 1-7 0.15-0.3 mol%	Cl +	R P H OH OH
1.0 0.55		94-99% ee	78-85% ee
equiv. equiv		40-49% y	42-50% y

Entry	Catalyst	$\mathrm{Mol} \%^a$	Time (h)	Ee $(\%)^{b}$
1	1	0.3	3	99
2	1	0.15	7	98
3	2	0.3	5	82
4	2	0.15	10	80
5	3	0.3	5	89
6	3	0.15	10	90
7	4	0.3	5	95
8	4	0.15	10	94
9	5	0.3	3	99
10	5	0.15	8	99
11	6	0.3	5	82
12	6	0.15	10	81
13	7	0.3	4	98
14	7	0.15	8	95

^aCatalyst loading as per Co unit w.r.t. racemic epoxide.

^bPercentage ee of product was analyzed by chiral GC or HPLC.

catalysts 1 and 5 at different substrate/catalyst molar ratios, and the results are summarized in Fig. 1. The catalyst loading has significant influence on catalytic activity and reaction rate. When the catalyst amount was increased from 0.05 mol% to 0.3 mol%, the reaction rate was greatly enhanced, and high enantioselectivity (99% ee) of epoxide was obtained within 3 h. On the other hand, the low loading (0.05 mol%) amount of catalyst exhibited 98% ee, when the reaction was prolonged, even with a low-loading catalyst. However, the Jacobsen's catalyst also retained the 99% enatioselectivity using 0.3 mol% of catalyst, but a decrease in reaction rate was observed. In comparision, the bimetallic catalysts 1 and 5 exhibited a similar enantioselectivity (99% ee) relative to heterometallic catalyst Co-AI^[10c] using 0.3 mol% within 3 h. It is very interesting to note that the catalyst 1 displayed 99% ee using 0.15 mol% at 15 °C within 12 h. On the basis of these all observations, it became clear that the heterometallic catalyst required two cobalt units, whereas the bimetallic catalyst required only one cobalt unit to attain high enantioselectivity. From a practical point of view, 0.3 mol% of catalyst is the optimal condition for the reaction. Importantly, the identity of second transition-metal salts in the catalyst was a critical parameter for high enantioselectivity and fast reaction



Figure 1. Catalytic activities of chiral Co (salen) complexes 1 and 5 with heterometallic cobalt salen complexes in the asymmetric HKR of (\pm) -ECH using 0.05 to 0.3 mol% catalyst, reaction at rt. $-\nabla$ - Cat. 1 (0.05 mol%), $-\Delta$ - Cat. 5 (0.05 mol%), $-\Delta$ - Cat. 1 (0.3 mol%), $-\Box$ - Cat. 5 (0.3 mol%), $-\times$ - Jacobsen cat. (0.3 mol%), $-\bigcirc$ - Cat. 1 (0.15 mol%, 15 °C), $-\bigstar$ - Cat. 1 (0.2 mol%, 15 °C), $-\bullet$ - Cat. 1a (0.5 mol%, Ref. [10c]), $-\Box$ - Cat. 1b (0.5 mol%, Ref. [10c]).

rate. Therefore, the present bimetallic catalytic system is more convenient than the previous report.d^[10c] The order of reactivity for the Co (salen) complexes is as follows: 1 > 5 > 4 > 7 > 3 > 6 > 2.

The scope of substrates was further explored using chiral Co (salen) complexes, and the most significant results are summarized in Table 2. As is evident from Table 2, the HKR was applicable to a wide variety of ether-containing epoxides. Methyl glycidyl ether, ethyl glycidyl ether, and isopropyle glycidyl ether all underwent resolution in excellent yield employing 0.3 mol% of catalysts under solvent-free conditions (Table 2, entries 1-3). Epoxides containing carbonyl functionalities were also examined as substrates for the HKR reaction. The kinetic resolution of glycidyl propionate and glycidyl butyrate (Table 2, entries 4 and 5) were efficient reactions, requiring 0.3 mol% of catalyst 5 within 4 h and affording recovered epoxide in 40% yield. The HKR of styrene epoxide was also performed successfully using 1.0 mol% of catalyst but required a longer reaction time to attain high enantiomeric excess (entry 6). Other aromatic epoxides such as phenyl glycidyl ether and their m-Cl and m-CH₃ derivatives also displayed excellent enatioselectivity using 0.3 mol% of catalyst (7-9). For the asymmetric ring opening of terminal epoxides, the high asymmetry-inducing

	(<i>R</i> , <i>R</i>)-Cat. 5		ОН
$\overset{O}{\longrightarrow}$ + H ₂ O	0.3-1.0 mol%	+	OH
R (±)	rt, 3-7 h	R	Ŕ
1.0 0.55		95-99% ee	> 85% ee
equiv. equiv.		40-49% y	42-50% y

Entry	Isolated product	Catalyst $(mol\%)^a$	Time (h)	Yield (%)	Ee $(\%)^b$
1		0.3	3	43	99
2		0.3	3	49	98
3		0.3	4	40	99
4		0.3	4	40	98
5		0.3	4	40	99
6	° ^	1.0	7	42	96
7		0.3	5	40	98
8		0.3	5	40	95
9		0.3	5	40	96

Table 2. Enantioselective HKR of various terminal epoxides using chiral Co (salen) complexes

^{*a*}Catalyst loading as per Co unit w.r.t. racemic epoxide.

^bPercentage ee of product was analyzed by chiral GC or HPLC.

ability of salen catalyst in this work could be attributed to the intense interaction of the substituent of salen ligand near the center metal atom as well as the attached metal atom with incoming substrate, indicating the cooperative reaction pathway.

A kinetics study of the HKR of (\pm) -ECH was carried out by considering the two-term rate equation^[11] involving both intra- and intermolecular components, and the results are summarized in Figure 2. Analysis of such plots with the rate data obtained with bimetallic catalysts **1** and **5** depicted linear correlation with positive slope and nonzero y-intercepts, consistent with both inter- and intramolecular pathways in the ring opening of epoxides with H₂O.^[11,12] The analysis of rate data obtained with Co(III)–NBS and Jacobsen catalyst revealed zero y-intercepts, reflecting absence of first-order pathway of these complexes. With bimetallic catalyst **1**, a maximum value of rate constant was obtained with a nonzero intercept, showing the highest reactivity and enantioselectivity. Thus, the bimetallic catalyst provides cooperative action to reinforce the reactivity and selectivity relative to monomeric catalyst.

As described in Table 1, the catalysts 1, 4, 5, and 7 exhibited a higher level of reactivity than 2, 3, and 6. The catalytic activities of the salen catalysts were examined to investigate the effect of NBS treatment and the type of added metal salts. The variation of enantiomeric excess percentages with time in HKR of glycidyl butyrate and glycidyl-3-methylphenyl ether is shown in Fig. 3. For all catalysts, the racemic substrates were kinetically well resolved to give an optically pure epoxide within 12 h. The optically pure isomers of various glycidol derivatives could be obtained by HKR of



Figure 2. Initial rate kinetics for the asymmetric HKR of the ECH catalyzed by chiral Co (salen) complexes.



Figure 3. Comparision of reactivity and enatioselctivity of catalyst **5** and Co(III)-NBS in HKR of aliphatic and aromatic epoxides.

racemates using new salen catalysts containing transition-metal salts. These salen catalysts showed unique catalytic activities. Under a standard condition employing 0.3 mol% of catalysts and 0.55 equivalent of H₂O, various optically pure glycidyl ether and ester compounds could be recovered with more than 99% ee in 40–49% isolated yield as shown in Table 2. The NBS-treated cobalt salen has similar reactivity and enantioselectivity for the HKR of ECH relative to Jacobsen's catalyst, having -OAc as a counteranion. Only NBS-treated salen catalyst exhibited lower reaction rates than the catalyst with Zn(NO₃)₂. However, almost similar high enantioselectivity (up to 99% ee) was provided with prolonged reaction time using those salen catalysts.

The chiral Co (salen) complexes were characterized by extended X-ray absorption fine structure (EXAFS) and electron spectroscopy for chemical analysis (ESCA) analysis. EXAFS analysis can be used to determine the coordination number and bond length in the salen structure. To analyze the details of the measured spectra, curve fitting for the EXAFS (extended X-ray analysis for fine structure) spectra was carried out with theoretically calculated spectra using the FEFF6 program. In the present work, the ligands with phenolic oxygen in the planar position act as bidentates in complexing with a metal halide or metal nitrate. The complexes of Co(II) salen presumably retain an essentially planar structure when they act as ligands, but the second transition-metal atom attached to the oxygen of salen do not need to lie exactly in the same plane as the first metal atom and its four donor atoms.

EXAFS data for newly synthesized chiral Co (salen) complexes are shown in Table 3. The Co-O, Fe-O, and Ni-O bond lengths were 1.76 Å,

Table 3. EXFAS results of chiral Co (salen) complexes by curve fitting using FEFF6 program

Sample	Pair	$\mathbf{R}(\mathbf{\mathring{A}})^{a}$	CN^b	σ2 (pm2)
Co-CoCl ₂	Co-O	1.76	2.20	54
	Co-Cl	1.98	2.47	31
	Co-Co	2.46	1.38	63
Co-FeCl ₃	Fe-O	1.85	1.44	0
	Fe-Cl	2.20	3.10	50
	Fe-Co	2.98	1.01	8
Co-NiCl ₂	Ni-O	1.82	2.02	0
	Ni-Cl	1.96	2.11	122
	Ni-Co	2.79	1.08	85

^aBond length.

^bCoordination number.

1.85 Å, and 1.82 Å, and coordination numbers were about 2, 1, and 2. This coordination can be generated only from the attachment of transition-metals to oxygens of salen. In addition, Co-Cl, Fe-Cl, and Ni-Cl bond lengths of coordinating transition-metal salts were 1.98 Å, 2.20 Å, and 1.96 Å. These M-Cl bond lengths are different than those of M-O. The coordination numbers for metal to chloride ions are about 2, 3, and 2 respectively. These coordination values are well matched to those of treated original salts such as $CoCl_2$, FeCl₃, and NiCl₂. The molar ratio of cobalt in the salen structure to the transition-metal was controlled as 1:1 for each case in the synthesis steps. Also, that ratio was kept constant in the sample, confirmed as 1:1 by EXAFS analysis. In addition, for the typical sample of Co(II)-salen containing FeCl₃, two absorption peaks for cobalt and iron were found simultaneously in the Fig. 4 because of the presence of cobalt in the center of salen complex as well as FeCl₃ salt bridged with phenolic oxygen of salen complex **4**.

Furthermore, ESCA was used to analyze and identify the environment created by the attachment of transition-metal to the salen complex. ESCA spectra can also provide information about an element's chemical environment or oxidation state. The chemical environment of an atom affects the strength with which electrons are bound to it. Atoms associated with different chemical environments produce peaks with slightly different binding energies. From Table 4, we have selected the Co(II)-salen and Co(III)-OAc (Jacobsen catalyst) as reference samples for comparative study of salen structures. In the case of Co(II)-salen, the binding energys of Co(II) and oxygen atoms are 779.67 eV and 531.47 eV. The Jacobsen catalyst contains an -OAc anion after oxidation of Co(II) with acetic acid under air. During this treatment, cobalt is oxidized from +2 to +3, and there is no interaction



Figure 4. EXAFS spectrum of cobalt-salen (FeCl₃).

between that anion and oxygens in the salen structure. Therefore, the binding energies for oxygen must remain the same for both Co(II) ligand and Jacobsen catalyst (i.e., 531 eV). It is clear that the binding energy value of cobalt was shifted from higher to lower because of the change in oxidation from +2 to +3.^[13–15] In contrast, the observed binding energies of oxygen atoms in ESCA spectra shifted from 531 eV [for Co(II) ligand] to 532.60 eV and 532.29 eV in the Co-NiCl₂ and Co-Co(NO₃)₂ complexes. This result provides direct evidence for coordination of the transition-metal. However,

Table 4. Characterization of chiral Co (salen) complexes using electron spectroscopy for chemical analysis (ESCA) techniques

Sr. No	M-X	Co2p3	O1s
1	Co ^{II} -Salen	780.69	531.03
2	Co ^{III} -OAC	779.67	531.47
3	Co ^{II} -NiCl ₂	780.96	532.60
4	Co ^{II} -Co (NO ₃) ₂	780.83	532.29



Figure 5. ESI-MS spectrum of cobalt-salen (FeCl₃).

the binding energies for cobalt in those two complexes are 780.96 eV and 780.83 eV, providing almost the same value as that of Co(II)-salen. On the basis of these observations, the change in binding energy of the oxygen atom originated from the anchoring of the transition-metal to the oxygen of Lewis acidic action.

ESI-MS spectra of Co-FeCl₃ (4) catalyst provide direct evidence of the configuration and formation of bimetallic complex. Bimetallic complex 4 showed significant peaks at m/z = 762.6, as can be seen from Figure 5. The monomeric salen ligand (precatalyst) has the peaks at m/z = 603.7. This mass spectrum for the catalyst showed that bimetallic salen is not a physical mixture of Co(II) ligand and transition-metals.

In conclusion, we have explored efficient chiral Co-(salen) complexes for the hydrolytic kinetic resolution of various racemic terminal epoxides to build a valuable chiral intermediate. We hope these bimetallic natures of the complexes would catalyze other important asymmetric reactions in high yield with excellent enantioselectivity. Efforts are under way to elucidate the mechanistic details and other significant applications of this catalytic system.

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